Official

REMARKS

The amendments to the pages of specification will be seen to be purely editorial, to correct clerical errors and omissions. No new matter has thereby been added.

For the reasons developed below, it is respectfully requested that the double patenting and Section 103 rejections be withdrawn with respect to the amended claims.

The method described and claimed in the present application employs the expansion step of strip perforation as a deformation treatment, which is then immediately followed by an annealing heat-treatment to produce a grain boundary-engineered structure. None of the prior art references discloses or suggests such a perforation/heat-treatment combination of steps and, as shown in Example 1/Table 1 at p.p.9-10 of the present specification, the prior art methods do not yield F_{sp} < 50%. Only the procedure of following perforation (Ex) followed by immediate HT affords the desired improvement in corrosion properties. CRHTEx does not.

In the description of prior art at pages 1 and 2 of the present application, it is acknowledged that two-step continuous processes to produce perforated current collectors are well known in the art. The first step produces a coiled and, optionally, heat-treated strip.

The present invention is directed to the second step of the process, in which strip coils are transferred to another process-line where the perforation takes place. The point of the invention as noted at page 1, lines 10-15 and as seen from the experimental Examples, is that perforation is immediately followed by an applied heat-treatment, before any pasting or other downstream operation occurs.

Claim rejections under 35 U.S.C. s.103

JP 406267544 discloses a continuous process of making a Pb-Ca-Sn alloy foil by slab casting, followed by rolling, followed by pasting and curing at 60°C. The express objective of the invention is to improve adhesion between the grid and the active material (as well as to improve service life), by means of a curing treatment applied subsequent to pasting. This is to be contrasted with the present process which uses the very perforation step as the deformation treatment for cast strip or rolled strip, immediately followed by a recystallizing heat treatment (prior to pasting).

The "recrystallization" treatment in the process of JP 406267544 is actually a curing treatment, performed on the pasted grids at temperatures of 60°C or greater to effect a desired contraction of the grid. As described in JP 406267544, heat-treatment of the pasted plate (which must remain below 100°C to avoid water loss - cf Rao '025 at col.16, lines 30-45) - goes on for at least one day and is not part of the continuous forming process.

It is respectfully submitted that no combination of the Japanese abstract teachings with the disclosure of Tilman et al. could point one in the direction of the present invention. The paragraph bridging columns 1 and 2 in Tilman, referred to by the Examiner, describes a heat treatment which is applied to slabs of alloys on the "rolling line" i.e. prior to coiling, preferentially by hot-rolling. This deals with the aforementioned step (i) of the two-step process of making grids. Tilman is entirely silent on any expansion/perforation process as well as on any heat-treatment immediately following the expansion step. Consequently, neither the Japanese abstract nor Tilman suggests the essential step of method of the present invention.

Neither can JP 406267544 be combined in any way with Rao et al. to arrive at the present applicants' invention, because Rao, too, fails to suggest the application of a heat-treatment immediately following the perforation (prior to pasting). Rao describes a continuous method for making a SLI grid, involving direct casting of a Pb-Ag-alloy strip (without rolling), followed by expansion, pasting, flash drying and, like the Japanese reference, curing (see Fig. 4 of Rao and descriptive text).

The Rao patent concerns itself with a cast strip only, subjected to a curing heat-treatment following pasting and not the process of the present invention, which uses perforation as the deformation treatment on cast strip or rolled strip, followed immediately by heat treatment at temperatures between 100 and 300°C, so as to increase F_{sp}.

It is also instructive in this connection that at column 12, lines 25-30, Rao states that no recrystallization occurs in direct cast and expanded Pb of his invention. At column 12, lines 36-47, Rao allows that some recrystallization occurs as a result of excessive cold working in the rolled strip process, and this he considers to be inferior to the cast strip. In Rao, no consideration is given to performing a heat-treatment to obtain a fully recrystallized structure, with attendant enhanced special grain boundary content.

Finally, it is respectfully submitted that Myers also fails to bridge the gap between JP 40627544 or Rao et al. and the present invention. The Myers patent describes a process which consists of a plurality of rolling steps (up to eleven) followed by a single brief heat-treatment to activate the strengthening mechanism of the antimony-lead alloy strips of interest. As noted at column 3, lines 24-26 of Myers, that mechanism fails in the absence of sufficient arsenic in the alloys. Myers' process involves a roll-deformation followed by a heat-treatment before expansion into a grid (see col.5, line 66 to co.6, line 1).

Inasmuch as Myers applies numerous hot or cold plastic deformations, followed by a single heat-treatment of the strip at 180-252°C for up to 2.5 ,minutes and requires Sb and As to be present in the alloy, it is not surprising that the process does not lead to materials that are at all comparable in grain size, grain orientation and special grain boundaries with the present invention.

Double Patenting

Lehockey at el. discloses a method for processing Pb-based alloys by subjecting them to a cold deformation to achieve a thickness reduction from 30-80%, followed by an annealing treatment at 180-300°C and repeating the deformation/annealing cycle at least once. As with Tilman and with Myers, the heat treatment of Lehockey is applied to the material "on the rolling line". Lehockey at el. makes no suggestion of any "continuous" process involving perforation. That is not surprising, as the Lehockey process is in fact a batch process, which uses separate, repetitive cycles of deformation and heat treatment.

As outlined at column 2, lines 4-5 of Lehockey deformation under that process includes rolling, pressing, extruding, stamping and drawing but not as with the present invention, any expansion/perforation step.

Lehockey discloses a multiple deformation/heat-treatment cycle batch process characterized with at least 30% deformation, to produce electrowinning anode sheets or plates. Lehockey does not disclose the use of perforations as the cold work treatment, with deformations below 10% [see page 2, second paragraph of present specification], for the purpose of fabricating perforated current collectors using a continuous process, which continuous process requires a heat-treatment immediately following the perforation.

Conclusion

It is respectfully submitted that the method defined and claimed in the present invention includes a critical and beneficial combination of process steps not to be found anywhere in the prior art. Perforation/deformation immediately followed by annealing at a temperature suitable to effect recrystallization, yields surprising high levels of special grain boundaries with resulting superior properties in metallic current collectors prepared by the method.

Favourable reconsideration and allowance of amended claims 1-16 enclosed herewith are therefore earnestly solicited.

Respectfully Submitted,
Tomantschger, Klaus et al

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Two-step processes are frequently used to prepare perforated current collectors using a continuous approach. In the first step, flat solid sheets are produced by a variety of strip casting or slab casting followed by rolling processes. The flat solid strips produced are typically wound into coils. Coils are typically stored until needed.

In the second step the strip coils are transferred to another process-line where the perforation and usually the active material pasting take place. This process generally starts with an uncoiler that unwinds the flat solid lead coils and feeds the strip into a perforation apparatus. Commonly used perforation techniques include reciprocating expanders, rotary expanders and grid punching systems. In the case of expanders the lead strip is slit and stretched to form a continuous expanded mesh. In the case punching is employed, typically rectangular coupons are punched out of the strip to create a continuous perforated grid-like sheet. The perforation processes apply mechanical stress to the lead foil by stretching and/or pressing the base material, but in all cases the overall strip deformation, as expressed by the ratio of the strip thickness before and after the perforation are kept under 10%, typically under 7.5%. The perforated strip created by any one of the listed processes travels downstream in the process to a paster, typically followed by a flash cure oven and is then cut into individual grids in tab blanker and plate dividers.

To enhance the longevity of non-consumable electrodes, current collectors and other metallic articles used in electrochemical cells, a variety of metal, metal alloys and composites have been developed. They include lead, copper, nickel, aluminum, iron, silver, zinc, lithium and their respective alloys. In many applications the environment in which the metallic articles are exposed to is highly corrosive and research is conducted to enhance the stability, e.g. by reducing the corrosion induced weight loss and growth experienced, particularly when the metallic article is exposed to oxidizing potentials and corrosive electrolytes. As many of the batteries in question are mass-produced at high speeds, continuous

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Lehockey et al. In U.S. 6,086,691, assigned to the owner of the present application, describes lead and lead-alloy anodes for electrowinning metals such as zinc, copper, lead, tin, nickel and manganese from sulfuric-acid solutions, whereby the electrodes are processed by at least two repetitive cycles of cold deformation in the range of 30-80% and a heat treatment of 10-30 minutes at 180 to 300°C to induce recrystallization and to achieve at least 50%special grain boundaries.

Palumbo in C.I.P. Serial No. 08/835,926 (1999), also assigned to the owner of rights in the present application, describes lead and lead-alloys with enhanced creep and/or intergranular corrosion resistance, especially for lead-acid batteries. The lead-alloy is subjected to at least one processing cycle comprising cold working the lead alloy to reduce the thickness thereof by a substantial amount, preferably in excess of 10% and subsequently annealing the lead-alloy for a time and temperature sufficient to effect recrystallization to substantially increase the special grain boundary fraction.

It is a teaching common to the prior art on the manufacture of current collectors that any mechanical deformation imposed during metal strip perforation/expansion has a detrimental effect on the corrosion performance of the resulting perforated current collector structure. In other words, it has been commonly understood to be a requirement for the optimization of corrosion performance that mechanical deformation at that stage of manufacture be minimized or eliminated.

However, the two above-noted commonly assigned patent applications do teach the use of substantial mechanical deformation, followed by a heat-treatment appropriate for the specific application, to recrystallize the grain structure.

The inventors of the present invention have discovered that the mechanical stress and much more limited deformation imposed on a metal strip in the usual application of a perforation process at near-ambient temperature to perforate the

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the melting point of the metal-alloy to yield a recrystallized microstructure. The deformation inherent in perforating the precursor metal strip, followed by annealing and recrystallization, increases the special grain boundaries in the microstructure, to the benefit of operating properties of the final article, i.e. the metallic current collector. The best properties are obtained when conditions are applied that raise the level of special grain boundaries in the microstructure to at least 50%.

Description of the Preferred Embodiment

Metallic current collectors, made from lead, copper, nickel, aluminum, iron, silver, zinc, lithium and their respective alloys, are well known in the art of electrochemical cell designs and a variety of forms, shapes and sizes, manufactured using a variety of processing techniques are employed. Most continuous processes used in e.g. the production of lead-acid battery grids rely on producing a coil of a flat solid strip using various commercially available processes.

Scientists continue to explore means of enhancing the corrosion performance of current collectors used in electrochemical cells typically exposed to electrolyte at various electrochemical potentials. Various metal, metal alloys and composites have been used in a variety of applications to improve longevity. Means of enhancing the corrosion properties by employing new compositions, surface coatings and treatments have also been described.

As is known by those skilled in the metallurgical art, cold working involves mechanical deformation of an article at a low enough temperature that dislocations are retained, leading to a structure of nonrecrystallized, deformed grains. This invention relies on cold-working the article by a strip expansion or punching process, resulting in strip thickness reduction of less than 10%, typically less than 7.5% and more typically less than 5%, followed by a suitable annealing treatment below the melting point of said metal or alloy.

Table 1:

Pb, 0.029% Ca, 0.73% Sn, 0.062%Ag, 0.035", 20 days
Various processes with and without heat-treatment of mesh

	CEx	CExHT	CREx	CRExHT	CRHTEx	CRHTExHT
Weight loss [mg/cm^2]	73	56	88	43	82	65
Vertical Growth [%]	6.2	1.1	7.7	0.2	3.3	1.6
Area Growth [%]	8.9	2.1	8.0	0.8	0.5	2.0
F_{sp} [%]	29	64	15	81	37	65
	Cast Control	Invention	Cast/Roll Control	Invention	Cast/Roll Heat Treatment Control	Invent

In Table 1, the column headings, C, R, Ex and HT stand for cast, rolled, expanded and heat treated, respectively. Thus, for example, the data in the fourth column relate to a sequence of processing in which a casting step is followed by a rolling step which is followed by an expansion step and, finally, a heat treatment step, according to the present invention.

Example 2

A lead strip was produced using conventional strip forming techniques. The nominal composition of the alloy was 0.036% Ca, 0.63% Sn, 0.036%Ag, the remainder being Pb. The strip was gravity cast to 0.080", then rolled to 0.040". The 0.040" lead-alloy strips were all heat-treated at 250 °C for 10 minutes. Thereafter the strips were cooled down to room temperature and rotary expanded to form a mesh as described in Example 1. No thickness reduction of the strip occurred in the expander. A portion of the mesh was subsequently heat-treated at 250 °C for 10minutes. Representative samples were corrosion tested as described in Example 1. Table 2 lists the results:

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Pb, 0.036% Ca, 0.63% Sn, 0.036%Ag, 0.040", 20 days

	Vertical Plate Plate Growth [%]	Plate Weight Loss Loss [mg/cm^2]	Fsp [%] Web
Control (CRHTEx)	9.0	67	22
This Invention (CRHTExHT)	2.4	44	68

Example 3

A lead strip was produced by extrusion and heat treated for 10 minutes at 250°C. Thereafter the strip was rolled to a final thickness of 0.035". The nominal composition of the alloy was 0.09% Ca, 1.25% Sn, the remainder being Pb. The lead-alloy strip was subsequently fed into a rotary expander as described in Example 1. A portion of the mesh was subsequently exposed to a heat-treatment at 250°C for 10minutes. Bare grid samples were subjected to a standard corrosion test as described in Example 1. Table 3 lists the results:

Table 3:

Pb, 0.09% Ca, 1.25% Sn, 0.035", 20 days

	Vertical Plate Plate Growth [%]	Plate Weight Loss Loss [mg/cm^2]	Fsp [%] Web
Control (XHTREx)	8.1	82	15
This Invention (XHTRExHT)	1.5	51	81

Similar results were obtained when the reciprocating expansion or punching was used to perforate the strip. In-line heat-treatment times of 30 seconds to one minute were determined to be sufficient in most cases to obtain the desired recrystallized structure. Suitable materials processed this way include lead, copper, nickel, aluminum, iron, silver, zinc, lithium and their respective alloys. In the case of lead strip, suitable alloying elements used were selected from the group of Ca, Sr, Ba, Sb, As, Al, Sn, Ag and Bi.

We Claim:

1. A method of manufacturing a metallic current collector for use in an electrochemical or galvanic cell, comprising the steps of:

(i) perforating a solid, flat metal strip using a continuous process that results in deformation of the strip at least locally near the perforations; and

(ii) Immediately following step (i), annealing the perforated strip at a temperature below the melting point of said metal or metal-alloy to yield a recrystallized microstructure therein.

2. A method according to claim 1, wherein said recrystallized microstructure contains a minimum of 50% special grain boundaries.

3. A method according to claim 1, wherein said continuous process is a process of reciprocating expansion.

4. A method according to claim 1, wherein said continuous process is a process of rotary expansion.

5. A method according to claim 1, wherein said continuous process comprises punching perforations through said metal strip.

6. A method according to claim 1, wherein said metal is selected from lead or a lead alloy.

7. A method according to claim 2, wherein said metal is selected from lead or a lead alloy.

Two-step processes are frequently used to prepare perforated current collectors using a continuous approach. In the first step, flat solid sheets are produced by a variety of strip casting or slab casting followed by rolling processes. The flat solid strips produced are typically wound into coils. Coils are typically stored until needed.

In the second step the strip coils are transferred to another process-line where the perforation and usually the active material pasting take place. This process generally starts with an uncoiler that unwinds the flat solid lead coils and feeds the strip into a perforation apparatus. Commonly used perforation techniques include reciprocating expanders, rotary expanders and grid punching systems. In the case of expanders the lead strip is slit and stretched to form a continuous expanded mesh. In the case punching is employed, typically rectangular coupons are punched out of the strip to create a continuous perforated grid-like sheet. The perforation processes apply mechanical stress to the lead foil by stretching and/or pressing the base material, but in all cases the overall strip deformation, as expressed by the ratio of the strip thickness before and after the perforation are kept under 10%, typically under 7.5%. The perforated strip created by any one of the listed processes travels downstream in the process to a paster, typically followed by a flash cure oven and is then cut into individual grids in tab blanker and plate dividers.

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